

Critical Exponents for Supercooled Liquids

Ethan Dyer,¹ Jaehoon Lee,¹ and Sho Yaida¹

¹*Center for Theoretical Physics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

We compute critical exponents governing universal features of supercooled liquids through the effective theory of an overlap field. The static correlation length diverges with the Ising exponent; the dynamical correlation length grows more rapidly; and the relaxation time obeys a generalized Vogel-Fulcher-Tammann form.

It is a longstanding problem to quantitatively characterize dramatic dynamical slowdown of supercooled liquids. Using the formalism developed in [1], we compute three critical exponents defined through

$$\xi_{\text{static}} \sim \Delta T^{-\nu}, \quad (1)$$

$$\xi_{\text{dynamic}} \sim \Delta T^{-\theta}, \quad (2)$$

$$\text{and } \log(\tau_\alpha) \sim \Delta T^{-\zeta}. \quad (3)$$

The results [cf. Eqs.(22)-(24)] can be tested against experiments and simulations.

Let us start by briefly reviewing the formalism. By doubly-replicating a system and defining a coarse-grained overlap field ϕ , various observables of a single supercooled liquid are imprinted onto the effective theory of an overlap field [1]. The static correlation length ξ_{static} of the overlap field serves as a proxy for the typical size of cooperatively rearranging regions ξ_{CRR} required for the supercooled liquid to access distinct amorphous configurations [2]. It is then stipulated that relaxation of the overlap field constitutes a thermal activation process, mediated by instantons. The size of this thermal instanton defines a dynamical length scale ξ_{dynamic} , a proxy for the typical size of mega rearrangements ξ_{M} required for the system to erase coarse memories [3]. The energy cost of these instantons characterizes the metastable lifetime τ_{meta} , a proxy for the relaxation time scale τ_α .

Envisioning that the number of accessible amorphous configurations becomes nonextensive near the Kauzmann temperature [4], we presume that the static correlation length diverges at a finite temperature $T_0 > 0$. The effective Hamiltonian near the critical temperature T_0 is then argued to lie in the Ising universality class. Specifically, as $\Delta T \equiv T - T_0 \rightarrow +0$ and after sufficient coarse-graining, the effective Hamiltonian approaches that of the Ising model with its near critical temperature $r \sim T^{\text{Ising}} - T_c^{\text{Ising}} \sim -\Delta T < 0$ and its external magnetic field $h \sim \Delta T^n$ (see Fig.1). Here n is required by analyticity to be a positive integer. An additional constraint on n comes from phenomenologically demanding that the effective Hamiltonian hold a metastable state. As we shall see, this gives rise to the relation $n \geq 2$ in all spatial dimensions $d > 1$. With the quick review passed us, we now determine the critical exponents for supercooled liquids.

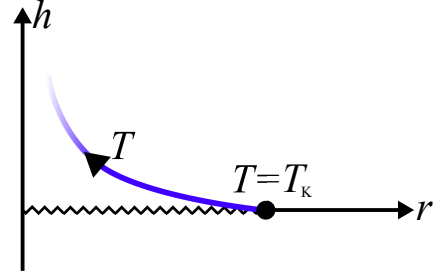


FIG. 1: A schematic picture of the line in the relevant parameter space of the Ising universality class, onto which our effective field theory projects. The dot denotes the unstable Ising fixed point where $(r, h) = (0, 0)$ and the zigzag line marks the first-order phase transitions. The line approaching the fixed point is given by $(r, h) \sim (-\Delta T, \Delta T^n)$ as $\Delta T \rightarrow +0$ [1].

For $d > 4$, we have the effective Hamiltonian

$$\frac{\mathcal{H}[\phi(\mathbf{x})]}{k_B T} = \int d^d \mathbf{x} \left[\frac{1}{2} (\nabla \phi)^2 + \frac{r}{2} \phi^2 + \frac{u}{4} \phi^4 + h \phi \right] \quad (4)$$

where u approaches a positive constant as $\Delta T \rightarrow +0$. Before embarking on the instanton calculation, it is useful to rescale the variables as

$$\tilde{\mathbf{x}} \equiv |r|^{\frac{1}{2}} \mathbf{x} \quad \text{and} \quad \tilde{\phi} \equiv u^{\frac{1}{2}} |r|^{-\frac{1}{2}} \phi, \quad (5)$$

so that the Hamiltonian takes the dimensionless form

$$\frac{\mathcal{H}[\tilde{\phi}(\tilde{\mathbf{x}})]}{k_B T} = \frac{1}{g} \int d^d \tilde{\mathbf{x}} \left[\frac{1}{2} (\tilde{\nabla} \tilde{\phi})^2 - \frac{1}{2} \tilde{\phi}^2 + \frac{1}{4} \tilde{\phi}^4 + \tilde{h} \tilde{\phi} \right] \quad (6)$$

where

$$g \equiv u |r|^{\frac{d-4}{2}} \quad \text{and} \quad \tilde{h} \equiv u^{\frac{1}{2}} |r|^{-\frac{3}{2}} h. \quad (7)$$

The potential holds a metastable state for $\tilde{h} < \frac{2}{3\sqrt{3}}$ and this is guaranteed as $\Delta T \rightarrow +0$ if and only if $n \geq 2$. Now, a thermal instanton $\tilde{\phi}_{\text{inst}}(\tilde{\mathbf{x}})$ is a dominant saddle configuration which interpolates between the metastable minimum $\tilde{\phi}_{\text{meta}}$ and the true minimum of the potential. It characterizes the leading metastable lifetime as [5]

$$\tau_{\text{meta}} \sim \exp \left(\frac{\Delta \mathcal{H}_a}{k_B T} \right) \quad (8)$$

with the activation energy

$$\Delta \mathcal{H}_a = \mathcal{H}[\tilde{\phi}_{\text{inst}}(\tilde{\mathbf{x}})] - \mathcal{H}[\tilde{\phi}_{\text{meta}}]. \quad (9)$$

As $\Delta T \rightarrow +0$ with $n \geq 2$, the parameter \tilde{h} approaches zero, making the calculation tractable as the thin-wall approximation [5, 6] becomes asymptotically exact [16]. In terms of the rescaled coordinates $\tilde{\mathbf{x}}$, the instanton configuration has a thin-wall at radius

$$\tilde{R}_{\text{inst}} \sim |\tilde{h}|^{-1}. \quad (10)$$

Within the wall the field transitions between the two minima and outside is nearly constant. The activation energy of this configuration is given by

$$\Delta \mathcal{H}_a \sim g^{-1} |\tilde{h}|^{-(d-1)}. \quad (11)$$

Converting back to the original coordinates \mathbf{x} , we thus obtain

$$\xi_{\text{static}} \sim |r|^{-\frac{1}{2}} \sim (\Delta T)^{-\frac{1}{2}}, \quad (12)$$

$$\xi_{\text{dynamic}} \sim |r|^{-\frac{1}{2}} |\tilde{h}|^{-1} \sim (\Delta T)^{-\{1+(n-2)\}}, \quad (13)$$

and

$$\log(\tau_\alpha) \sim g^{-1} |\tilde{h}|^{-(d-1)} \sim (\Delta T)^{-\{d-\frac{5}{2}+(n-2)(d-1)\}}. \quad (14)$$

The previous mean-field scaling argument holds only for spatial dimensions $d > 4$. For $d < 4$, the would-be perturbative parameter g , governing higher order corrections, diverges near the critical point [7]. We instead need to employ a renormalization-group scaling argument [17].

For $1 < d < 4$, let us again parametrize by r the relevant thermal direction and by h the relevant magnetic direction of the Ising universality class (cf. Fig.1). Under the renormalization group transformation, the thermal activation picture implies that

$$I(r, h) \equiv \log(\tau_{\text{meta}}) \quad (15)$$

has a simple scaling relation near the critical point. As we rescale the distance by a multiplicative factor b ,

$$I(r, h) \approx I(b^{1/\nu_I} r, b^{\Delta'_I/\nu_I} h). \quad (16)$$

Here, $1/\nu_I$ and $\Delta'_I = \beta_I \delta_I$ are the thermal exponent and the gap exponent of the Ising model, respectively. We rescale until $b_\star^{1/\nu_I} r = r_{\text{MF}}$ with r_{MF} fixed well away from the critical point, where the mean-field picture is valid. In particular, defining $h_{\text{eff}} \equiv b_\star^{\Delta'_I/\nu_I} h$,

$$I(r_{\text{MF}}, h_{\text{eff}}) \sim |h_{\text{eff}}|^{-(d-1)} \quad \text{as } h_{\text{eff}} \rightarrow 0. \quad (17)$$

Note that

$$|h_{\text{eff}}| \sim |r|^{-\Delta'_I} |h| \sim (\Delta T)^{n-\Delta'_I} \quad (18)$$

approaches zero as $\Delta T \rightarrow +0$ if and only if $n > \Delta'_I$: as $\Delta'_I \approx 1.56$ for $d = 3$ and $\Delta'_I = \frac{15}{8}$ for $d = 2$, we again

ensure the metastability condition by demanding $n \geq 2$. Near the critical point, we then obtain

$$\xi_{\text{static}} \sim b_\star \sim |r|^{-\nu_I} \sim (\Delta T)^{-\nu_I}, \quad (19)$$

$$\xi_{\text{dynamic}} \sim b_\star |h_{\text{eff}}|^{-1} \sim (\Delta T)^{-\{\nu_I+(2-\Delta'_I)+(n-2)\}}, \quad (20)$$

and [18]

$$\log(\tau_\alpha) \sim |h_{\text{eff}}|^{-(d-1)} \sim (\Delta T)^{-\{(2-\Delta'_I)(d-1)+(n-2)(d-1)\}}. \quad (21)$$

Finally, plugging in the known values of the Ising critical exponents [11] yields

$$\begin{aligned} \nu &= \nu_I \\ &\approx 0.63 \quad \text{for } d = 3 \\ &= 1 \quad \text{for } d = 2, \end{aligned} \quad (22)$$

$$\begin{aligned} \theta &= \nu_I + (2 - \Delta'_I) + (n - 2) \\ &\approx 1.07 + (n - 2) \quad \text{for } d = 3 \\ &= \frac{9}{8} + (n - 2) \quad \text{for } d = 2, \end{aligned} \quad (23)$$

and

$$\begin{aligned} \zeta &= (2 - \Delta'_I)(d - 1) + (n - 2)(d - 1) \\ &\approx 0.87 + 2(n - 2) \quad \text{for } d = 3 \\ &= \frac{1}{8} + (n - 2) \quad \text{for } d = 2. \end{aligned} \quad (24)$$

The Ising exponent in the static correlation length has been observed in various numerical simulations [12, 13]. In response to these, Langer proposed an Ising-like theory [14]. Work along this line may provide, not only evidence for the static part of our formalism, but also a complementary picture.

As for the dynamics, we have $\theta > \nu$, indicating that the dynamic correlation length grows more rapidly than the static one. This “decorrelation” of static and dynamic length scales is numerically observed in [15]. It would be interesting to see if our prediction for θ can match experiments and simulations and, if it does, whether n is unique or labels different classes of supercooled liquids.

The relaxation time obeys a generalized Vogel-Fulcher-Tammann form,

$$\tau_\alpha \sim \exp \left[\left\{ \frac{E_0}{k_B(T - T_0)} \right\}^\zeta \right] \quad \text{as } T \rightarrow T_0, \quad (25)$$

with $\zeta \neq 1$. For $d = 3$, the minimal choice of $n = 2$ yields $\zeta \approx 0.87$, which is close enough to 1 that there is no apparent experimental conflict to our knowledge. It would be illuminating to check against extremely patient and accurate experiments in the future.

Even if the formalism withstands rigorous experimental tests, there will remain important questions. Do there

exist additional theoretical constraints on n ? More fundamentally, we assumed that the relaxation of the overlap field proceeds through thermal activation. It would be exciting to figure out what kind of stochastic dynamics, Langevin or otherwise, governs the overlap field and whether it indeed gives rise to the thermal activation picture.

We thank Daniel S. Fisher and Steven A. Kivelson for stimulating discussions on the dynamics, Alan H. Guth for discussion of bubble nucleation, and Stephen H. Shenker for helpful discussions on the renormalization group. We are also indebted to Allan W. Adams for moral support. J.L. is supported in part by Samsung Scholarship. S.Y. is supported by a JSPS Postdoctoral Fellowship for Research Abroad.

-
- [1] S. Yaida, arXiv:1212.0857 [cond-mat.dis-nn].
 - [2] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).
 - [3] J.-P. Bouchaud and G. Biroli, J. Chem. Phys. **121**, 7347 (2004).
 - [4] W. Kauzmann, Chem. Rev. **43**, 219 (1948).
 - [5] J. S. Langer, Ann. Phys. **41**, 108 (1967) [Ann. Phys. **281**, 941 (2000)]; Annals Phys. **54**, 258 (1969).
 - [6] For a review, see S. Coleman, *Aspects of Symmetry* (Cam-

- bridge University Press, Cambridge, 1985).
- [7] For a review, see N. D. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group* (Addison-Wesley, Reading, MA, 1992).
- [8] K. G. Wilson and J. B. Kogut, Phys. Rept. **12**, 75 (1974).
- [9] J. Rudnick and D. Nelson, Phys. Rev. B **13**, 2208 (1976).
- [10] A. Houghton and T. C. Lubensky, Phys. Lett. A **77**, 479 (1980).
- [11] A. Pelissetto and E. Vicari, Phys. Rept. **368**, 549 (2002) [cond-mat/0012164].
- [12] H. Tanaka, T. Kawasaki, H. Shintani, and K. Watanabe, Nature Mater. **9**, 324 (2010).
- [13] M. Mosayebi, E. D. Gado, P. Ilg, and H. C. Öttinger, Phys. Rev. Lett. **104**, 205704 (2010).
- [14] J. S. Langer, arXiv:1301.7019 [cond-mat.stat-mech].
- [15] P. Charbonneau and G. Tarjus, arXiv:1211.4821 [cond-mat.dis-nn].
- [16] As $g \ll 1$ near the critical point for $d > 4$, fluctuations contribute an innocuous subleading prefactor to τ_{meta} .
- [17] We note that the following scaling argument can be explicitly implemented in the framework of the ϵ -expansion [8], integrating out the degrees of freedom until the cutoff scale is of the same order as the correlation length scale [9]. The results agree at least to first order in ϵ [10].
- [18] Plugging in the mean-field value $\Delta'_1 = 3/2$ into Eq.(21) does not reproduce Eq.(14). This is due to the fact that the quartic term is dangerously irrelevant for $d > 4$ near the Gaussian fixed point.